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《Original》

A Study of Boron Determination in High Purity Aluminum by Capture Gamma-Ray Measurement

Nak Bae Kim and Hae-iLL BAK

Seoul National University

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즉발감마선 계측에 의한 고순도 알루미늄중의 붕소정량에 관한 연구

김 낙 배 · 박 혜 일

서울대학교

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Abstract

The boron content in reacter grade aluminum has been determined by means of a capture gamma-ray counting method. The experimental detection limit is found to be 5.7% ppm with 10% uncertainty. In order to improve the sensitivity, the boron is preconcentrated from aluminum by cation exchange resin system. The accuracies of both methods, i.e., one by the direct measurement and the other by the measurement after preconcentration, are checked by an additive method. The results show good agreements with less than 5% deviation.

요 약

중성자포획 감마선 방사화분석법을 이용하여 원자로급 알루미늄중 붕소를 분석하였다. 실험에 의한 검출한계는 10% 불확실도의 경우 5.7ppm 이었다. 함량이 더욱 미량인 경우를 위하여 양이온 교환수지를 이용하며 알루미늄으로 부터 붕소를 사전분리하는 농축법을 개발하였다. 이 두 방법 즉 직접 측정하는 방법과 농축후 측정하는 두가지 방법의 정확도를 첨가법으로 조사하였다. 그 결과 5% 편차 이내에서 잘 일치하였다.

1. Introduction

In the conventional neutron activation analysis, the delayed gamma-rays of radioisotopes produced by neutron bombardment are used to determine the elemental composition of a sample. The basic requirement for the method is that the produced nuclide is radioactive and has reasonable half-life. On the other hand, capture gamma-ray counting activation analysis is independent

of the products' nuclear characteristics. The capture of a neutron by a nucleus leads to the formation of an excited state and the immediate emission of one or more prompt particles or photons. In the case of thermal neutron capture, generally gamma-rays are produced. Certain elements such as B, S, P and some of rare earths, which have large neutron capture cross section and/or produce no suitable radioisotope, are not suitable for the conventional neutron activation analysis, but can be analyzed by the capture gamma-ray counting activation analysis.

Several workers have mentioned the use of neutron capture gamma-rays as an alternative technique for nondestructive elemental analysis.[1-23] Among these, the boron determination has been frequently studied but their detection limits[4,5,9,13,16] are relatively too high to determine the contents in reactor grade materials.

In the present work, a feasibility was studied for the determination of boron in reactor materials by nondestructive capture gamma-ray counting activation analysis and the lowering of the detection limit. In order to lower the detection limit of the method, the preconcentration of boron in aluminum was carried out by using cation exchange column[24,25,26].

2. Experimental

2-1. Experimental set-up

A collimated beam of neutron, 2.54cm in diameter, has been extracted out of the beam port of TRIGA Mark III reactor. A 20cm thick bismuth crystal placed in path of the beam helps to reduce the gamma-ray background from reactor. The thermal neutron flux at the target position is $1.2 \times 10^6 n \cdot cm^{-2} \cdot sec^{-1}$ and the cadmium ratio of gold is 13.

All the measurements are made by means of a 75cc Ge(Li) detector connected with 4096 channel analyzer(ORTEC Model 7044). The Ge(Li) detector was shielded with lead bricks of 10cm thickness and covered additionally by the mixture of paraffine and boric acid (30 weight %) of 10cm thickness. The front face of lead castle for the detector has a hole of 8.5cm diameter and is covered with 3m/m thick sintered borate plate with a hole of 12cm diameter. The diagram of this arrangement is shown in Fig. 1.

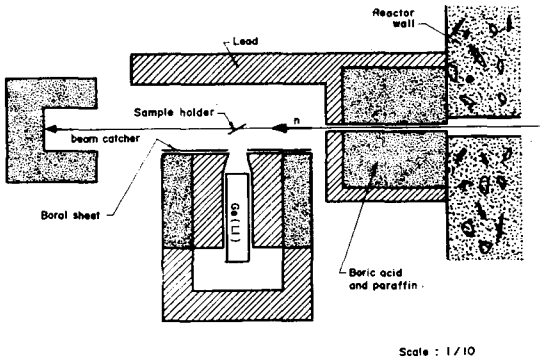

Fig. 1. Top View of the Capture Gamma-ray Apparatus

A sample holder was made by two thin polyethylene wires to minimize the scattering of neutron and background of gamma-ray. Two wires were fixed to cross at the pathway of neutron beam which is adjusted to have an angle of 90° with axis of the detector. The sample surface was adjusted by two wires, so as to have 45° angle both with neutron beam and with the axis of the detector.

2-2. Direct meansurement of capture gamma-ray

The standard boric acid sample was

prepared as follows.

Boric acid was dissolved in redistilled water and stored in a volumetric flask. A 100 lambda aliquot of the solution containing an appropriate quantity of boron was pipetted on a 3cm×3cm boron-free polyethylene sheet and dried by infra-red lamp. The sheet was folded carefully and inserted into a 2cm×2cm polyethylene bag.

The surface cleaned aluminum sample of 2cm×2cm×1m/m size and the boric acid standard were attached on the crossed point of polyethylene wires with 1.5cm×1.5cm Scotch tape. Each aluminum sample was irradiated and measured for 4000sec.

2-3. The preconcentration of boron

In order to improve the detection limit, the boron in aluminum sample was preconcentrated as follows.

An aluminum sample of suitable size was dissolved in a minimum amount of 6N hydrochloric acid in a quartz beaker. After dissolution, a few drops of H_2O_2 were added and heated gently for a few minutes to dissolve perfectly the residues and to destroy any organic materials. The solution was diluted more than 6 times with distilled water, and then passed through the cation exchange resin column in quartz tube[24,25] (Dowex 50×8, 50-100 mesh, 8cm diameter and 40cm height). The column was washed with 150m*l* of redistilled water. The flow rate was adjusted to 10m*l* per min. The eluates were collected in quartz beaker and 1m*l* of 3% mannitol solution was added to prevent the volatilization of boron during heating.[26] The solution was concentrated to 10m*l* by gentle heating. A 5m*l* aliquot was transferred on a 3cm×3cm polyethylene sheet step by step with 1m*l* a time and dried by infra-red lamp. And then the polyethylene bag containing separated boron was prepared similarly as for boron standard.

3. Results and Discussion

The well known reaction between ^{10}B and thermal neutrons,

$$^{10}B+n \begin{cases} \nearrow {}^{7}Li+{}^{4}He+2.8MeV \quad (7\%) \\ \searrow ({}^{7}Li)^{*}+{}^{4}He+2.3MeV\,(93\%), \end{cases} \qquad (1)$$

is extensively used in neutron physics both as a standard reaction for the calibration of cross section and as a method for the neutron detection. The cross section, 752 barns, of the reaction is known to better than 1% error[7,8] and its energy dependance follows strictly 1/v law up to 100keV, the first resonance occurring at 530keV.[1] The prominant gamma-energy produced in this reaction is 478keV.

A background spectrum, taken by the polyethylene wires and the Scotch tape of 1.5cm×1.5cm, is shown in Fig. 2. Most of low energy gamma-ray backgrounds can be seen to lie below 0.2 MeV. The peaks of ^{60}Co and ^{41}Ar such as 1.173, 1.332 and 1.293 MeV can be also seen as room backgrounds.

A 695 keV peak is due to an electron conversion transition in ^{72}Ge following inelastic neutron scattering and is broadened on account of the recoiling germanium ions.[4] The similar peaks are observed at 595keV, 867keV, 253keV, 296keV, 326keV, 609keV, 1101keV and 961keV with other small peaks due to the $^{74}Ge(n,n'\gamma)$ reaction. These peaks originate within the detector, as ^{74}Ge in the detector captures neutrons which are entered into the detector by scattering on the sample holder. The sample holder produces double escaping peak of 2232keV due to the capture reaction by hydrogen and the peaks of 517keV, 789keV and 1164

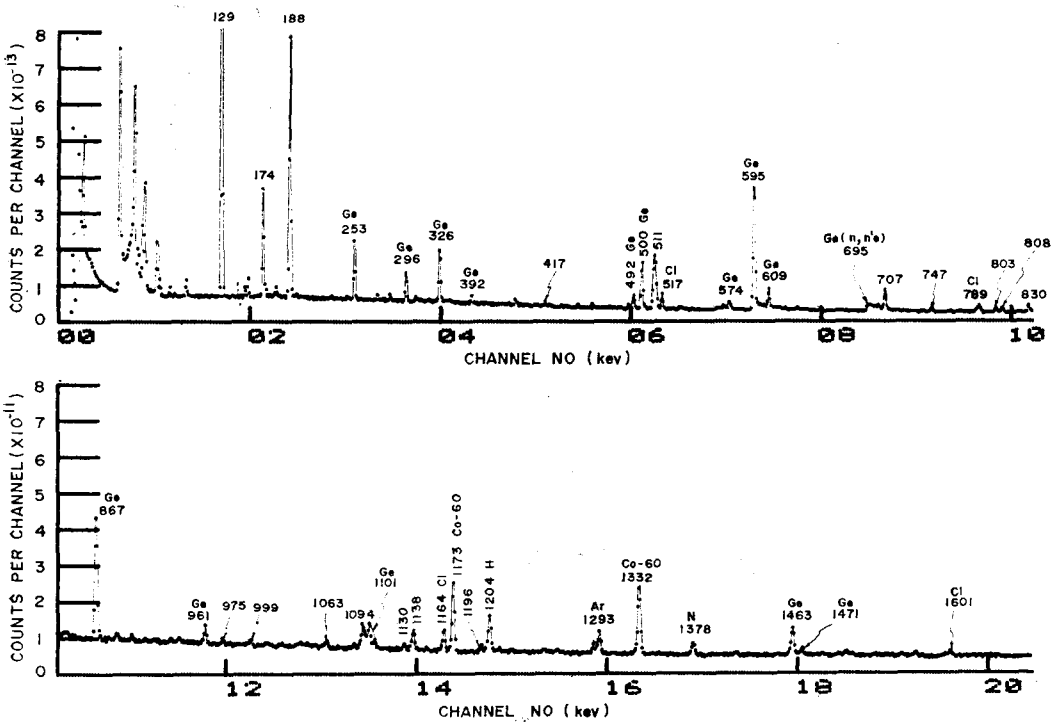

Fig. 2. The Background Spectrum with Polyethylene Wires and Scotch Tape in the Target Position

keV due to that by chloride in Scotch tape. But there are no peaks in the energy region of 470keV-486keV, which is provided for the capture reaction by boron.

The spectrum of 700μg boron standard is shown in Fig. 3, which is obtained after subtraction of background spectrum. Ninety-three percent of ^{7}Li produced by the ^{10}B $(n,\alpha)^{7}$Li reaction is in an excited state which decay with emitting a 478 keV prompt gamma-ray. Since the gamma-ray is emitted while the recoiling ^{7}Li nucleus is in flight, Doppler-effect makes the peak broaden. It can be calculated by the well known formula,

$$E_k=\frac{m}{M+m}\times 2.3\,(\mathrm{MeV}) \qquad (2)$$

$$D=\frac{v}{c}\cdot E_r\cdot\cos\theta=\sqrt{\frac{2E_k}{m}}\cdot\frac{E_r}{c}\cdot\cos\theta, \qquad (3)$$

where E_k is the kinetic energy of ^{7}Li, M is the mass of ^{7}Li, m is the rest mass of α-particle, D is Doppler-broadening, v is the velocity of $(^{7}\mathrm{Li})^{*}$, c is light velocity, E_r is gamma-ray energy and θ is the angle between the directions of gamma-ray and $(^{7}\mathrm{Li})^{*}$. This broadening is to be 15.3keV and is also shown in Fig. 3 that the distinctive rectangular energy distribution of the boron peak indicates a broadening of ~15keV. This result is agreed with other's[5].

A 3 gram of aluminum was counted for 4000sec and the spectrum obtained after the subtraction of background spectrum is shown in Fig. 4. As the neutron beam is scattered much more intensively on the sample than on the sample holder only, the photopeaks in the background spectrum

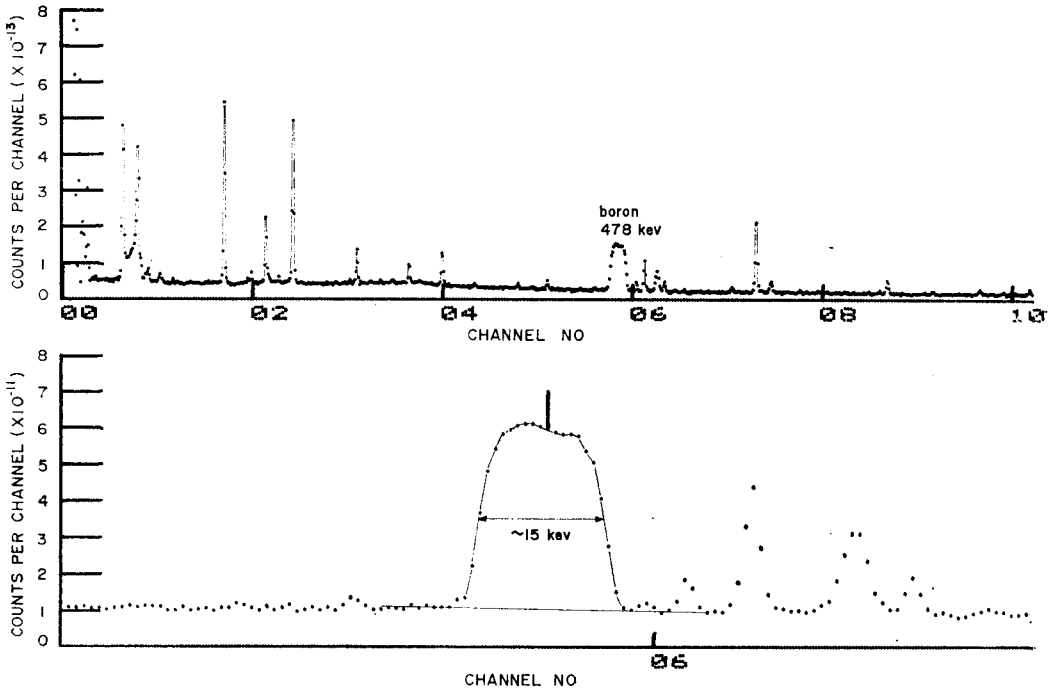

Fig. 3. Capture Gamma-ray Spectrum of 700μg Boron
upper: the spectrum after background substruction
lower: Doppler broadened boron peak

are still remained in the aluminum spectrum. The energies of the gamma-rays produced by the neutron capture reaction of aluminum are 249keV, 329keV, 758keV, 830 keV, 983 keV, 1014 keV and 1623 keV. All of these photopeaks except three photopeaks of 830keV, 249keV and 329keV are identified in Fig. 4. Those three peaks are overlapped with the photopeaks in the background spectrum. The broadened peak of boron is also seen in the spectrum of Fig. 4.

If the minimum detection limit is defined by Cooper[27], net count of the minimum detection, Nmin, is given as follows;

$$\mathrm{Nmin}=C\left\{\left(2B+\frac{C^2}{4}\right)^{1/2}+\frac{C}{2}\right\}, \qquad (4)$$

where C is the value of 100 divided by user set uncertainty (%) and B is the background, which includes both counts from the environment and the continuum from higher energy gamma-ray peaks. If the 10% uncertainty is allowed, Nmin is 3987 count and for 20% uncertainty, it is 1886 count. So the minimum detection limit of boron content is 17.1μg for 10% uncertainty, and 8.5μg for 20% uncertainty. These results is comparative to other's results[4,5,9,13,16], if their results are corrected by comparing the conditions of the neutron flux and the irradiation time used in the present work with their experimental condition.

The value of 17.1μg given above is found to be equivalent to 5.7ppm with 10% uncertainty. For the most of reactor grade materials, the boron content is much lower

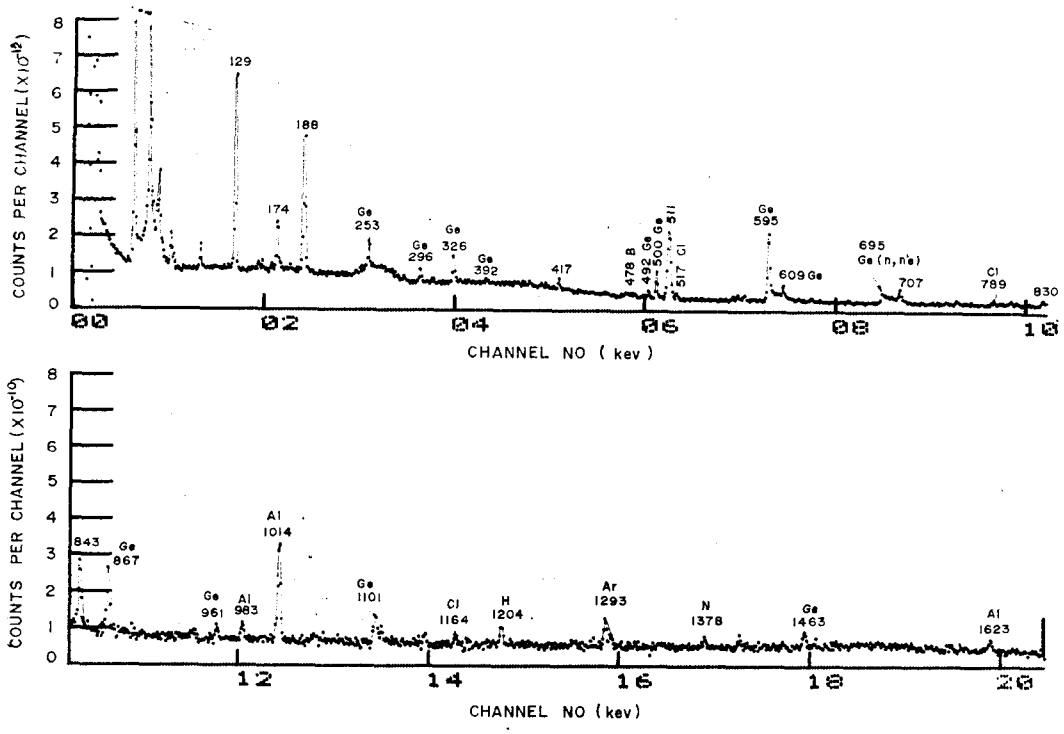

Fig. 4. Capture Gamma-ray Spectrum of Aluminum after Background Subtraction

than this detection limit.

In order to lower the detection limit further, the simple preconcentration method was developed. The recovery of boron during the separation with cation exchange column is over 98%, with agreement to others[24,25]. In the process of the concentrating the boron contained eluates by heating, an appropriate amount of the mannitol was added to prevent the loss of boron by evaporation.[26] The loss of boron in the concentrating process was not appeared, but without adding the mannitol the loss was more than 25%.

To determine the accuracy of the preconcentration method, an additive method was applied. A number of known amounts of boric acid was added to the solutions of 10 gram of aluminum, and the procedures

Table 1. The Relation between Mass of Boron and Count Rate.

mass of boron, μg, $\times 10^{-2}$ x	measured peak area of boron, $\times 10^{-4}$, with % uncertainty y
0.350	1.9481±2.5
0.701	2.6565±1.8
1.05	3.4340±1.5
1.40	4.0425±1.2
2.10	5.6905±0.9
2.80	7.4075±0.7

least square fit
$y=(2.22\pm0.038)x+(1.09\pm0.025)$

of "the preconcentration of boron" were carried out as described above and analyzed. The result is shown in Table1. The equation derived from least square fit to the data is

$$y=(2.22\pm0.038)x+(1.09\pm0.025), \quad (5)$$

where $y=$ peak area $\times 10^{-4}$ and $x=$ boron

mass$\times 10^{-2}$. The intercept on the y-axis is due to the content of boron in the sample and the slope is the peak area per μg of boron. The boron content in an aluminum sample calculated from these data is (49± 1.4) μg per 5 gram of Al, giving a divergence of only 5% compared with the value of the direct measurement. The analytical results of some aluminum samples are shown with a standard deviation in Table 2.

Table 2. Analytical Results of Boron Contents in Aluminum Samples.

sample	contents of boron (ppm), $\pm 1\sigma$	
	direct measure.	preconcentration
A1060	—	2.7±0.2
A1070	7.2±0.3	7.3±0.2
A6061	9.8±0.3	10.1±0.3
Commercial	15.1±0.6	14.9±0.2

It is easily understood by the other report[4] that the error occurring by the flux depression in sample is negligible, because the amount of the preconcentrated sample is very small and because the amount of aluminum sample is not so thick as to make the flux depression. The variation in thermal neutron flux also shows a little fluctuation with 0.3% standard deviation during carring out the present work.

In conclusion, the detection limit of boron is found to be 5.7ppm with 10% uncertainty when the aluminum sample is measured directly. The detection limit can be further lowered to 0.57ppm when a 30g quantity of aluminum is treated.

This method could be easily applied to other materials such as metals and uranium compounds.

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